

A SINGLE CRYSTAL EPR STUDY OF THE PLATINUM (III)-BIS (MALEONITRILEDITHIOLATE)-MONOANION

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Abstract—A first single crystal EPR study of a Pt^{3+} chelate—tetrabutylammonium—bis (maleonitriledithiolato) platinate (III)—diamagnetically diluted by the corresponding gold (III) chelate is reported. The spectra are described by a rhombic spin Hamiltonian. For some orientations of the magnetic field ^{33}S superhyperfine splitting was observed. The ^{33}S tensor has the maximum value perpendicular to the plane of the complex supporting a $^2B_{3g}$ ground state in which the half-filled out-of-plane π molecular orbital is extensively delocalized over the ligands. Furthermore, the electron spin-lattice relaxation of the Pt^{3+} complex was measured in the temperature range $4.2 \leq T \leq 16$ K. Spin-lattice interactions were found to be mainly responsible for the linewidth in the Pt^{3+} spectra, which is larger by a factor 2 than those observed for Pd^{3+} and Ni^{3+} in the same host complex $[\text{Au}(\text{mnt})_2]^-$.

INTRODUCTION

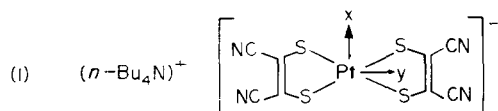
During the last years several single crystal EPR studies were made on transition metal dithiolene complexes in which unusual oxydation states of the metal ions are stabilized [1–6]. Due to the small linewidths usually observed for these complexes in the spectra small hyperfine interactions could be resolved what provides direct information about the nature of the electronic ground state and the extent of electron spin delocalization over ligand orbitals. Until now only very few data are available for Pt^{3+} chelates [7–10]. In this paper we report the first single crystal EPR study on a complex containing three-valent platinum: tetra-*n*-butylammonium-bis (maleonitriledithiolato) platinate (III), (*n*-Bu₄N) $[\text{Pt}(\text{mnt})_2]$ (I). Besides of the ^{195}Pt hfs (hfs = hyperfine structure) the maximum splitting of the ^{33}S ligand hfs could be resolved, furthermore, some results of our spin-lattice relaxation studies on the present system are discussed. To our knowledge up to now there are no results concerning the electron spin-lattice relaxation of Pt^{3+} [11].

on 2% Pt^{3+} (relative to Au^{3+}) containing crystals with a 28.8 GHz spectrometer as described earlier [12] in the temperature range $4.2 \leq T \leq 16$ K using the pulse saturation technique. The pulse width was varied between 200 μs and 2 ms. The signal klystron power entering the cavity was $\approx 1 \mu\text{W}$; the ratio of the power of the saturation pulses to the signal-klystron power was $\approx 10^5$.

Unfortunately, exact structural data of (*n*-Bu₄N) $[\text{Pt}(\text{mnt})_2]$ and (*n*-Bu₄N) $[\text{Au}(\text{mnt})_2]$ are unknown. However, the general features of the angular dependence of the *g* tensors of both magnetically nonequivalent sites present in the unit cell agree with those of the system $\text{Ni}^{3+}/[\text{Cu}(\text{mnt})_2]^-$ studied by Schmitt and Maki [2]. The same was found for the system $\text{Pd}^{3+}/[\text{Au}(\text{mnt})_2]^-$ [6]. Therefore, one may conclude that the crystal structures of the Pt^{3+} , Pd^{3+} and Au^{3+} chelates are similar to those of the corresponding Ni^{3+} and Cu^{3+} chelates which have a monoclinic unit cell with two structural units.

RESULTS

The EPR spectra of $[\text{Pt}(\text{mnt})_2]^-$ show in addition to an intense central line (66.3% of the Pt isotopes have a zero nuclear spin) the expected Pt hfs line doublet, caused by the interaction of the unpaired electron with the ^{195}Pt nucleus (^{195}Pt , nuclear spin $I = \frac{1}{2}$, natural abundance 33.7%). In general the single crystal spectra depict the absorption signals of two magnetically non-equivalent molecules. In Figs. 1 and 2 the spectra for the magnetic field directions $H \parallel x$ and $H \parallel y$ are reproduced. When rotating the crystal around the axis for which both structural units of the unit cell are magnetically equivalent, the direction of the minimum *g* tensor component (*g*_z) comes within approx. 3° of being coincident with the magnetic field direction. The same was observed for the $\text{Ni}^{3+}/[\text{Cu}(\text{mnt})_2]^-$ system [2] and also for $\text{Pd}^{3+}/[\text{Au}(\text{mnt})_2]^-$ [6]. Therefore, this rotation axis can be assumed as being identical with the crystallographic *b* axis. The EPR spectra can be described by a rhombic-symmetric spin Hamiltonian (1)



EXPERIMENTAL

Single crystals of tetra-*n*-butylammonium-bis (maleonitriledithiolato) aurate (III), (*n*-Bu₄N) $[\text{Au}(\text{mnt})_2]$, containing approx. 2% (*n*-Bu₄N) $[\text{Pt}(\text{mnt})_2]$ were grown by slow evaporation of a $\text{CH}_2\text{Cl}_2/\text{CHCl}_3$ solution. Well-formed black crystals were obtained without difficulties.

The EPR spectra were recorded at $T = 295$ K and 4.2 K in the X-band (at 9.4 GHz) with a JEOL "JES-3BQ" and a VARIAN E 112 spectrometer. The principal values of the *g* and the ^{195}Pt tensor were derived as described earlier [6]. The magnetic field was calibrated with NMR markers; *g* values were derived using DPPH as reference.

Measurements of the spin-lattice relaxation time *T*₁ were made

$$\hat{H}_{sp} = \beta_e \sum_{i=x,y,z} g_i H_i \hat{S}_i + \sum_{i=x,y,z} \hat{S}_i A_i \hat{I}_i \quad (1)$$

whose parameters are summarized in Table 1.